Thermally stable C₆₀ nanowires on Si substrates

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We have formed C_{60} nanowires on Si substrates using selective adsorption of C_{60} at the steps on the Si(111) $\sqrt{3}$ -Ag surface. The use of the misoriented Si(111) wafer enabled us to produce an array of C_{60} nanowires of 2–5 nanometers in width and height and more than one micrometer in length. The nanowire produced was found to tolerate high-temperature processing of up to 700°C, therefore the Ag atoms on the surface could be removed while leaving the C_{60} nanowires on the Si(111) substrate.

Introduction

Nanoscale carbon materials such as carbon fullerenes and nanotubes are very attractive because they can be metallic, semiconducting, or superconducting, and because they are composed of the most abundant material on earth.¹⁾ For the last decade, therefore, extensive work has been carried out to investigate the properties of carbon materials.¹⁾ Recently, researchers have been searching for the ways to manipulate carbon materials in device structures $^{2-6)}$ for the fabrication of future nanoscale devices.

Some of the important factors for utilizing nanoscale carbon materials in actual devices would be the uniformity and purity of the material itself. In this sense, the C₆₀ molecule is a good candidate because it has become the most well-purified and mass-produced nanoscale carbon material after the work of Krätschmer *et al.*⁷⁾ In this review, we show how a C₆₀ nanowire can be formed on a semiconductor surface and discuss about its thermal stability.⁸⁾

Experimental

C₆₀ nanowires were formed in an ultrahigh-vacuum chamber equipped with a scanning tunneling microscope (STM) as follows. First, a clean Si(111)7 × 7 surface was prepared by annealing at 650°C for 24 h followed by repeated annealing at 1250°C for a few seconds. The Si(111)7 × 7 surface was converted to Si(111) $\sqrt{3}$ × $\sqrt{3}R30^\circ$ -Ag [referred to as Si(111) $\sqrt{3}$ -Ag hereafter] by depositing one monolayer of Ag at appropriate temperatures.⁹⁾ C₆₀ molecules were deposited onto the Si(111) $\sqrt{3}$ -Ag surface at 200 or 400°C, resulted in a selective adsorption of C₆₀ along steps. The deposition of C₆₀ on the same surface at room temperature yielded film growth on the terraces in addition to the adsorption at the steps.^{10, 11} All the STM observations in this study were performed at room temperature using electrolytically etched Pt-20%Ir or W tips.

Results and discussion

Figure 1 (a) shows an STM image (scan area of 200 nm \times 200 nm) acquired after depositing C₆₀ on the Si(111) $\sqrt{3}$ -Ag surface at 200°C. This image indicates that C₆₀ adsorbs preferentially at surface steps rather than on the terraces. Here, the amount of C₆₀ molecules supplied was controlled to be



Fig. 1. (a) STM image showing selective adsorption of C₆₀ molecules on Si(111) $\sqrt{3}$ -Ag at a substrate temperature of 200°C. Arrows in the image indicate 2D clusters of C₆₀ molecules. (b) STM image of the surface after annealing the sample at 400°C for 20 min.

the same as that required to cover the surface with one monolayer of C_{60} at room temperature,¹¹⁾ suggesting that most of the molecules were desorbed from Si(111) $\sqrt{3}$ -Ag during deposition.

As indicated by red and blue arrows in Fig. 1 (a), two types of two-dimensional (2D) clusters of C_{60} were also formed. According to our STM observations at higher resolution, the first type (red arrows) has a random molecular arrangement while the second type (blue arrows) has a nearly hexagonal molecular arrangements as reported previously.¹¹) Figure 1 (b) shows another STM image obtained after additional

annealing at 400°C for 20 min. We note that different areas are imaged in Figs. 1 (a) and (b). In these two STM images, we can see that the C₆₀ molecules decorating the steps remain firmly on the surface while the 2D clusters of C₆₀, indicated by blue arrows in Fig. 1 (a), desorb from the surface upon annealing at 400°C. The 2D clusters of C₆₀, indicated by red arrows in Fig. 1 (a), however, do not disappear after the annealing at 400°C [see Fig. 1 (b)]. Such a stable 2D cluster of C₆₀ was found to be formed if Si(111)7×7 regions are retained on the Si(111) $\sqrt{3}$ -Ag surface prior to the deposition of C₆₀; this indicates that the C₆₀ molecules in the stable 2D clusters are directly bound to Si dangling bonds.

The model for the growth of C_{60} on the Si(111) $\sqrt{3}$ -Ag surface is schematically shown in Fig. 2. A C_{60} molecule on the Si(111) $\sqrt{3}$ -Ag surface diffuses on the terrace, and it is trapped at a line defect on the surface, such as a step or an out-of-phase boundary (OPB),⁹⁾ as well as at a point defect on the terrace. The growth of the C_{60} monolayer is initiated only adjacent to the steps,¹¹⁾ as shown in Fig. 2. It is interesting to note that, within the range of our experiments, the C_{60} molecules trapped at point defects on a terrace do not act as nucleation sites for monolayer growth. As observed in Figs. 1 (a) and (b), the C_{60} molecules at defects (steps, OPB's, and point defects) are stable while those on a terrace are less stable.

Now, let us devise a method of fabricating high-quality one-dimensional structures consisting of C_{60} molecules (C_{60} nanowire). The most important point is to reduce densities of OPB's and point defects on a Si(111) $\sqrt{3}$ -Ag surface. In other words, to form C_{60} nanowire using selective adsorption at steps, defects other than the surface steps must be avoided. Another point to be considered is how to make the isolated C_{60} nanowires. This latter point becomes very important in the measurement of the conductivity of the fabricated C_{60} nanowires.



Fig. 2. A model for the growth of C₆₀ on the Si(111) $\sqrt{3}$ -Ag surface.

In order to fulfill the above requirements, we used the misoriented Si(111) wafer (4° off toward the [11 $\overline{2}$] direction) as a substrate and deposited Ag atoms on Si(111)7×7 at temperatures in a range of 500–600°C. In this temperature range, the size of the Si(111) $\sqrt{3}$ -Ag domain easily exceeds one micrometer,¹²⁾ so OPB's are not formed within that domain size. The use of the misoriented Si(111) wafer is helpful not only for realizing an array of C₆₀ nanowires without intersections between the nanowires but also for improving the quality of the Si(111) $\sqrt{3}$ -Ag surface due to suppression of the "hole-island" growth of Ag on Si(111).¹³⁾

Figure 3 (a) shows an STM image (200 nm \times 200 nm) of an array of C₆₀ nanowires formed along the surface steps on the misoriented Si(111) substrate. In this case, C₆₀ was deposited on the Si(111) $\sqrt{3}$ -Ag surface at 400°C in order to prevent unnecessary adsorption as much as possible, and then the sample was further annealed at 700°C for 1 min. As we see in Fig. 3 (a), there were neither intersection between C₆₀ nanowires nor 2D clusters of C₆₀ on the surface, because a Si(111) $\sqrt{3}$ -Ag surface nearly free of defects was prepared on the misoriented Si(111) substrate.

Each C_{60} nanowire is about 2–5 nm in height and in width at maximum. Unfortunately, it is rather difficult to perform a more precise evaluation from the present STM observations. This is because the conventional STM tip used here is not able to follow the exact shape of the bunched step where the



Fig. 3. (a) An array of C_{60} nanowires fabricated on the Si substrate. There are neither intersections between C_{60} nanowires nor 2D clusters of C_{60} molecules on the surface. (b) Cross-sectional profile measured along the diagonal line from the upper left to the lower right corner of (a).

present C_{60} nanowire is formed. The length of the nanowire free of any intersection or junction with another nanowire was typically longer than one micrometer.

Figure 3 (b) shows a cross-sectional profile of the same sample as shown in Fig. 3 (a). From this profile, the heights of the steps [*H* in Fig. 3 (b)] are measured to be 2–3 nm, indicating that each step is not a single step (0.32 nm in height) of the Si(111) substrate but a cluster of six to ten single steps (referred to as a bunched step hereafter). The spacings between the bunched steps [*L* in Fig. 3 (b)] are measured to be 20– 50 nm in Fig. 3 (b). The averaged value of $\tan^{-1}(H/L)$ for the present sample was 3.8 degrees which is in good agreement with the specified angle of misorientation (4 degree) for the Si(111) wafer used here.

Finally, we discuss the thermal stability of the C_{60} nanowires. As described above, the C_{60} nanowires shown in Fig. 3(a) were annealed at 700°C, therefore, these nanowires can tolerate high-temperature processing of up to 700°C. Furthermore, the present annealing conditions resulted in a complete removal of Ag atoms from the Si(111) $\sqrt{3}$ -Ag surface. Actually, the surface in Fig. 3 (a) shows the $Si(111)N \times N$ surface structure, where the observed value for N was not only 7 but also 3, 5, 9, and 11. This $N \times N$ surface structure is characteristic when the $Si(111)\sqrt{3}$ -Ag surface is converted to the bare Si(111) surface by Ag desorption at 700°C. This result indicates the importance of the created C_{60} nanowire in the measurement of electrical resistance and for realizing nanodevices, since we can oxidize the underlying silicon substrate in order to insulate the nanowire from the conductive substrate.¹⁴⁾

Summary

We presented a method of forming C_{60} nanowires on a Si substrate. By using selective adsorption of C_{60} at the steps on the Si(111) $\sqrt{3}$ -Ag surface and by adopting a misoriented Si(111) wafer, an array of C_{60} nanowires was fabricated. It was found that the nanowires produced can tolerate hightemperature processing of up to 700°C, therefore the Ag atoms on the surface could be removed completely while leaving the C_{60} nanowires on the Si(111) substrate.

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